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(54) **AMPHIPHILIC MACROMOLECULE AND USE THEREOF**

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C09K 8/12 (2006.01)

C09K 8/62 (2006.01)

C09K 8/03 (2006.01)

C09K 8/58 (2006.01)

C09K 8/68 (2006.01)

C08F 220/28 (2006.01)

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CPC **C08F 220/56** (2013.01); **C08F 220/28** (2013.01); **C09K 8/03** (2013.01); **C09K 8/12** (2013.01); **C09K 8/58** (2013.01); **C09K 8/62** (2013.01); **C09K 8/68** (2013.01); **D21H 17/375** (2013.01); **D21H 21/18** (2013.01)

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USPC **526/303.1**, **287**, **305**, **307.2**, **307.3**; **162/168.3**; **507/120**, **225**

See application file for complete search history.

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(57) **ABSTRACT**

Amphiphilic macromolecules having repeating structural units: structural units to adjust molecular weight and molecular weight distribution and charging property effects, high stereo-hindrance structural units, and amphiphilic structural units, and are suitable for fields such as oil field well drilling, well cementation, fracturing, oil gathering and transfer, sewage treatment, sludge treatment and papermaking, etc., and can be used as an oil-displacing agent for enhanced oil production, a heavy oil viscosity reducer, a fracturing fluid, a clay stabilizing agent, a sewage treatment agent, a papermaking retention and drainage aid or a reinforcing agent, etc.

15 Claims, 1 Drawing Sheet

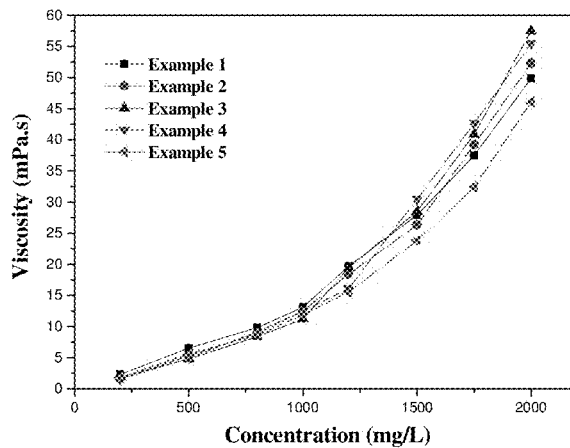


Figure 1: The relationship between the viscosity and concentration

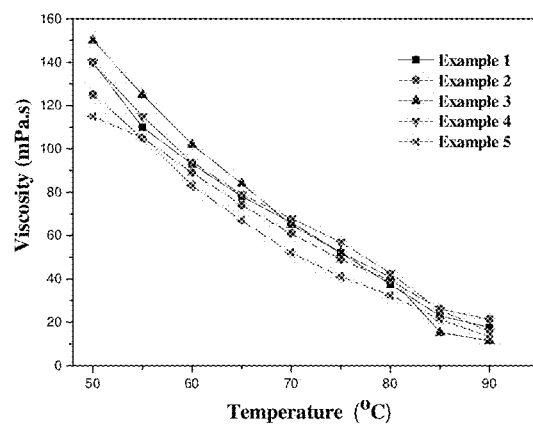


Figure 2: The relationship between the viscosity and temperature

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AMPHIPHILIC MACROMOLECULE AND USE THEREOF

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a national stage entry of PCT/CN2011/001579 filed Sep. 16, 2011, which claims priority to Chinese Patent Application No. 201110210362.X, filed on Jul. 26, 2011, said applications are expressly incorporated herein in their entirety.

TECHNICAL FIELD

This invention relates to an amphiphilic macromolecule and uses thereof, and this amphiphilic macromolecule is applicable to oilfield drilling, well cementing, fracturing, crude oil gathering and transporting, sewage treating, sludge treating and papermaking, and it can be used as intensified oil producing agent and oil displacing agent, heavy oil viscosity reducer, fracturing fluid, clay stabilizer, sewage treating agent, retention aid and drainage aid and strengthening agent for papermaking.

BACKGROUND OF THE INVENTION

Chemical flooding is one of the most effective and potential chemical technologies for Enhanced Oil Recovery, which is especially represented by polymer flooding. However, there arise some problems for conventional polymers along with the deep implementation of polymer flooding technology. Under reservoir conditions of high temperature and high salinity, the viscosifying capacity and thermal stability of the widely used polymer, partially hydrolyzed polyacrylamide (HPAM), reduces rapidly; in the meantime, HPAM does not have the surface/interfacial activity per se, and could not start the oil film effectively, so that its ability to mine the remaining oil is limited. The polymer-based binary-component composite system (polymer/surfactant) and triple-component system (polymer/surfactant/alkali) may enhance the stability of the emulsified produced fluid, resulting in increased difficulty in oil/water separation and sewage treatment, as well as the weakening of synergistic effect among the components of the system under reservoir conditions, and also it may damage the reservoir. The application of the composite system is thus restricted.

It has become a difficulty and key for many large oilfield developments to keep the viscosifying capacity and viscosity stability of the polymer solution, so as to achieve the strategic target of stabilization of oil production and water cut control.

Heavy oil is a collective name for unconventional oil, including heavy oil, high viscosity oil, oil sand, natural asphalt and etc., and they are also referred to as heavy oil, ultra-heavy oil, asphalt and etc. Among the approximate 10 trillion barrels of remaining oil resources around the world, more than 70% of which is heavy oil resource. Chinese onshore heavy oil and bitumen resources account for about more than 20% of their total oil resources. According to incomplete statistics, the proved and controlled heavy oil reserves in China reach 1600 million tons. Nowadays heavy oil resource has become one of the important strategic replacement resources in China; however, the exploitation of heavy oil is rather difficult. Chemical emulsification and viscosity reduction method has become an important exploitation technology.

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Polymeric emulsification viscosity reducer usually refers to a polymeric surfactant with a relative molecular weight more than several thousands and significant surface activity; according to the ion types, it can be divided into four categories: anionic, cationic, zwitterionic and non-ionic polymeric surfactant. Polymeric surfactant usually has limited capacity to reduce surface tension and oil-water interfacial tension, but has excellent emulsification and dispersion capability for heavy oil, with advantages of small usage amount, high viscosity reduction rate, lower cost and simple implementation process. In recent years, this research especially attracts more and more attention in this field.

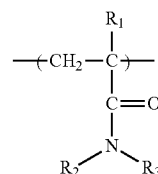
BRIEF DESCRIPTION OF THE INVENTION

In the following context of this invention, unless otherwise defined, the same variable group, and molecular and structural formula have the same definitions.

The instant invention relates to an amphiphilic macromolecule, this amphiphilic macromolecule has repeating units as described below: a structural unit A for adjusting molecular weight, molecular weight distribution and charge characteristics, a highly sterically hindered structural unit B and an amphiphilic structural unit C.

In an embodiment, the structural unit A for adjusting molecular weight, molecular weight distribution and charge characteristics comprises (meth)acrylamide monomer unit A₁ and/or (meth)acrylic monomer unit A₂. Preferably, the structural unit A includes (meth)acrylamide monomer unit A₁ and/or (meth)acrylic monomer unit A₂ simultaneously. In the art, the molecular weight of the amphiphilic macromolecule may be selected as needed, preferably, this molecular weight may be selected between 1000000-20000000.

Preferably, the (meth)acrylamide monomer unit A₁ has a structure of formula (1):



formula (1)

In formula (1), R₁ is H or a methyl group; R₂ and R₃ are independently selected from the group consisting of H and a C₁-C₃ alkyl group; R₂ and R₃ are preferably H.

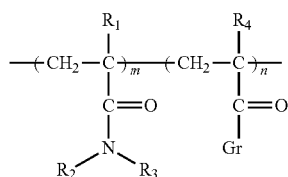
Preferably, the (meth)acrylic monomer unit A₂ is (meth)acrylic acid and/or (meth)acrylate. Preferably the (meth)acrylate is sodium methacrylate.

Preferably, the molar percentage of (meth)acrylamide monomer unit A₁ in the whole amphiphilic polymer repeat units is 70-99 mol %; preferably 70-90 mol %, more preferably 70-80 mol %.

Preferably, the molar percentage of (meth)acrylic monomer unit A₂ in the whole amphiphilic polymer repeat units is 1-30 mol %; preferably 1-28 mol %, more preferably 20-28 mol %.

In another embodiment, the structural unit A for the regulation of molecular weight, molecular weight distribution and charge characteristics has a structure of formula (2):

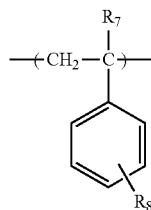
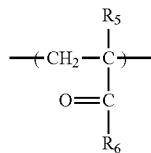
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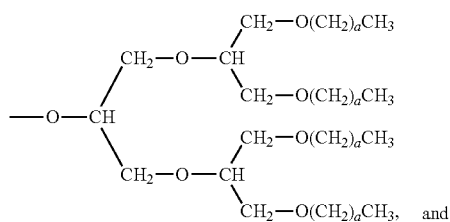
wherein, R_1 is H or a methyl group; R_2 and R_3 are independently selected from the group consisting of H and a C_1 - C_3 alkyl group; R_2 and R_3 are preferably H; R_4 is selected from H or a methyl group; Gr is ---OH or $\text{---O}^-\text{Na}^+$; m and n represent the molar percentage of the structural units among the entire amphiphilic macromolecule repeating unit, and m is 70-99 mol %, preferably 70-90 mol %, more preferably 70-80 mol %; n is 1-30 mol %, preferably 2-28 mol %, more preferably 20-28 mol %.

In another embodiment, in formula (2), R_1 - R_3 is preferably H, Gr is preferably $\text{---O}^-\text{Na}^+$.

In another embodiment, the highly sterically hindered structural unit B contains at least a structure G, wherein the structure G is a cyclic hydrocarbon structure formed on the basis of two adjacent carbon atoms in the main chain, or is selected from a structure of formula (3), and the highly sterically hindered structural unit B optionally contains a structure of formula (4):



In formula (3), R_5 is H or a methyl group; preferably H; R_6 is a radical selected from the group consisting of the structures of formulas (5) and (6).

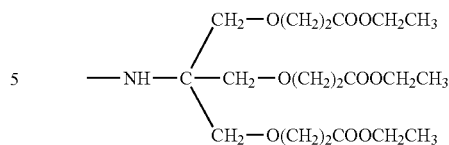


Formula (2)

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formula (6)

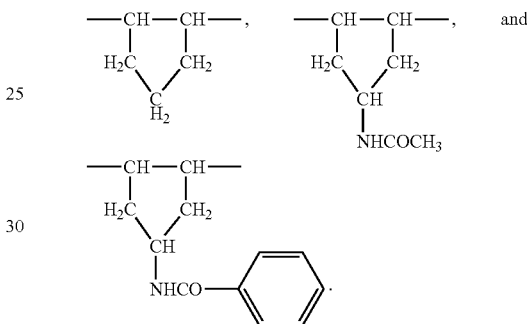


In formula (5), a is an integer from 1 to 11; preferably 1-7;

In formula (4), R_7 is H; R_8 is selected from H, $\text{---SO}_3\text{H}$ and salts thereof, $\text{---}(\text{CH}_2)_2\text{CH}_2\text{Cl}$, $\text{---CH}_2\text{N}^+(\text{CH}_3)_2(\text{CH}_2)_\xi\text{CH}_3\text{Cl}^-$ or $\text{---CH}_2\text{N}^+(\text{CH}_3)_2(\text{CH}_2)_2\text{N}^+(\text{CH}_3)_2(\text{CH}_2)_\sigma\text{CH}_3\text{Cl}^-$; ξ and σ are respectively integers from 1 to 15, preferably 1-11.

Preferably, the highly sterically hindered structural unit B comprises a structure G and a structure of formula (4).

In another embodiment, the cyclic hydrocarbon structure formed on the basis of two adjacent carbon atoms in the main chain is selected from the group consisting of:

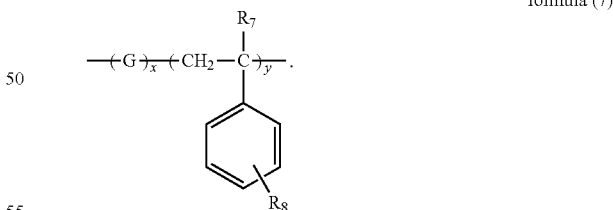


formula (3)

Preferably, the molar percentage of structure G of the highly sterically hindered structural unit B in the entire amphiphilic macromolecule repeating units is 0.02-2 mol %; preferably 0.02-1.0 mol %, more preferably 0.05-0.5 mol %.

Preferably, the molar percentage of the structure of formula (4) of the highly sterically hindered structural unit B in the whole amphiphilic polymer repeat units is 0.05-5 mol %; preferably 0.1-2.5 mol %, more preferably 0.15-0.75 mol %.

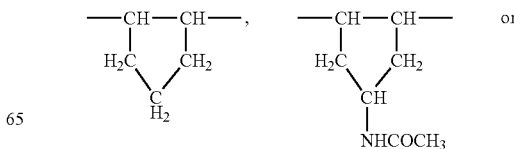
In another embodiment, the highly sterically hindered structural unit B has a structure of formula (7):



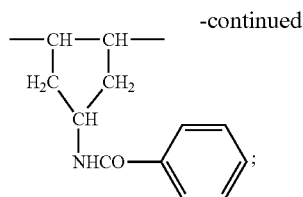
formula (7)

formula (5)

In formula (7), the definition on G is as described above, preferably the structure of formula (3),

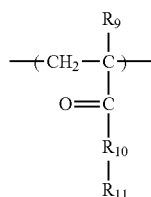


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the definitions on R_7 and R_8 are as described in formula (4); x and y represent the molar percentages of the structures in the entire amphiphilic macromolecule repeating units, and x is 0.02-2 mol %, preferably 0.02-1.0 mol %, more preferably 0.05-0.5 mol %; y is 0.05-5 mol %, preferably 0.1-2.5 mol %, and more preferably 0.15-0.75 mol %.

In another embodiment, the amphiphilic structural unit C has a structure of formula (8):



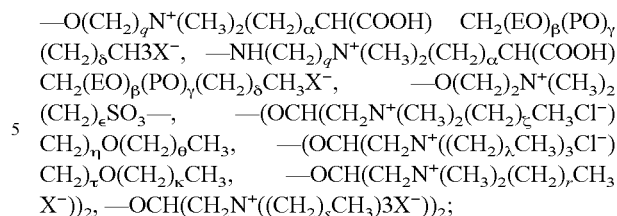
formula (8)

In formula (8), R_9 is H or a methyl group; R_{10} is $-\text{O}-$ or $-\text{NH}-$; R_{11} is a radical containing a straight-chain hydrocarbyl, a branched hydrocarbyl, a polyoxyethylene (PEO) group, a polyoxypropylene (PPO) group, an EO and PO block, a mono-quaternary ammonium salt, a multiple-quaternary ammonium salt or a sulfonic acid and salts thereof.

Preferably, the molar percentage of the amphiphilic structural unit C in the entire amphiphilic macromolecule repeating units is 0.05-10 mol %; preferably 0.1-5.0 mol %, more preferably 0.2-1.7 mol %.

In another embodiment, the structures consisted of R_{10} and R_{11} can be selected from $-\text{O}(\text{CH}_2)_g\text{N}^+(\text{CH}_3)_2(\text{CH}_2)_h\text{CH}_3\text{X}^-$, $-\text{NH}(\text{CH}_2)_i\text{N}^+(\text{CH}_3)_2(\text{CH}_2)_j\text{CH}_3\text{X}^-$, $-\text{O}(\text{CH}_2)_k\text{N}^+((\text{CH}_2)_l\text{CH}_3)_p\text{X}^-$, $-\text{O}(\text{CH}_2)_q\text{N}^+(\text{CH}_3)_2(\text{CH}_2)_\alpha\text{CH}(\text{SO}_3\text{H})\text{CH}_2(\text{EO})_\beta(\text{PO})_\gamma(\text{CH}_2)_\delta\text{CH}_3\text{X}^-$, $-\text{NH}(\text{CH}_2)_q\text{N}^+(\text{CH}_3)_2(\text{CH}_2)_\alpha\text{CH}(\text{SO}_3\text{H})\text{CH}_2(\text{EO})_\beta(\text{PO})_\gamma(\text{CH}_2)_\delta\text{CH}_3\text{X}^-$,

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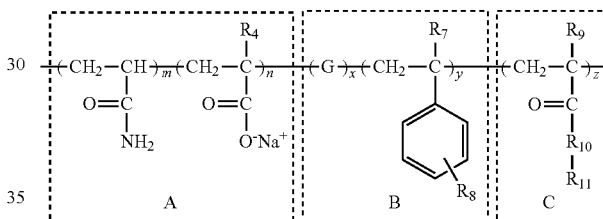


wherein, g , i , k and q are respectively integers of 1-6, preferably 2-4; h and j are respectively integers of 3-21, preferably 3-17; p is an integer of 3-9, preferably 3-5; α is an integer of 1-12, preferably 1-8; β and γ are respectively integers of 0-40, β is preferably 0-25, γ is preferably 0-15; δ is an integer of 0-21, preferably 0-17; ϵ is an integer of 4-18, preferably 4-12; ζ is an integer of 1-21, preferably 1-15; η and τ are respectively integers of 1-30, preferably 1-20; θ and κ are respectively integers of 3-21, preferably 3-17; λ is an integer of 0-9, preferably 0-5; r is an integer of 3-21, preferably 3-17; s is an integer of 3-9, preferably 3-5; and X^- is Cl^- or Br^- .

In another embodiment, the amphiphilic macromolecule has a structure of formula (9):

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Formula (9)

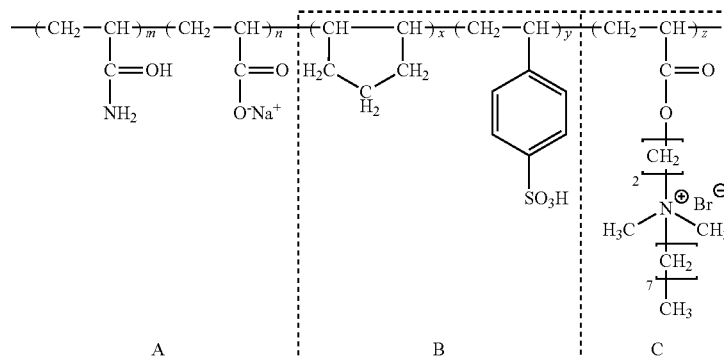


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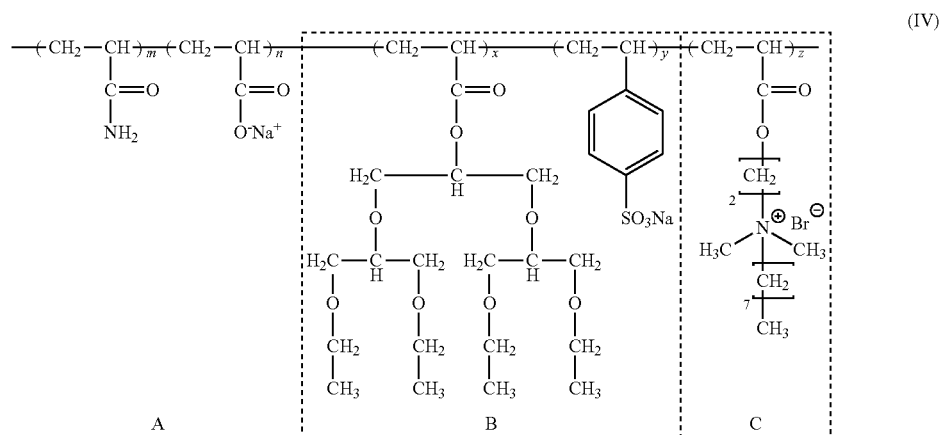
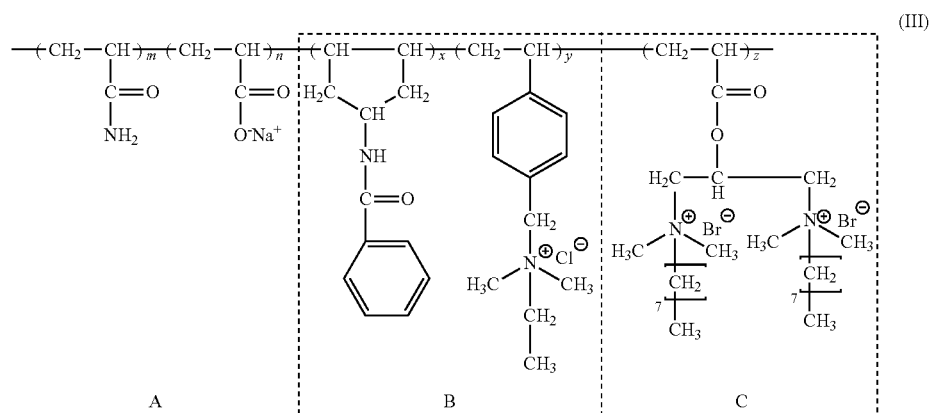
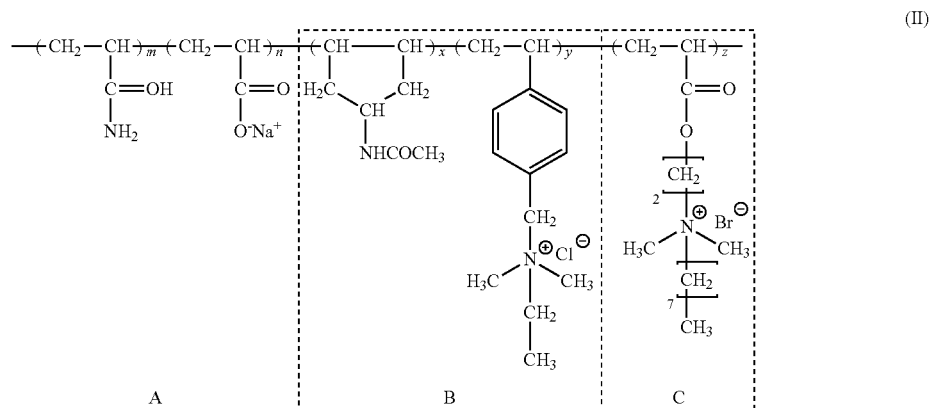
In formula (9), the definitions on R_4 , m and n are as described in formula (2); the definitions on R_7 , R_8 , G , x and y are as described in formula (7); the definitions on R_9 , R_{10} and R_{11} are as described in formula (8); z represents the molar percentage of this structural unit in the entire amphiphilic polymer repeat unit, and z is 0.05-10 mol %, preferably 0.1-5.0 mol %, more preferably 0.2-1.7 mol %.

Specifically, this present invention provides a high molecular compound having a structure of formulas (I)-(X):

(I)



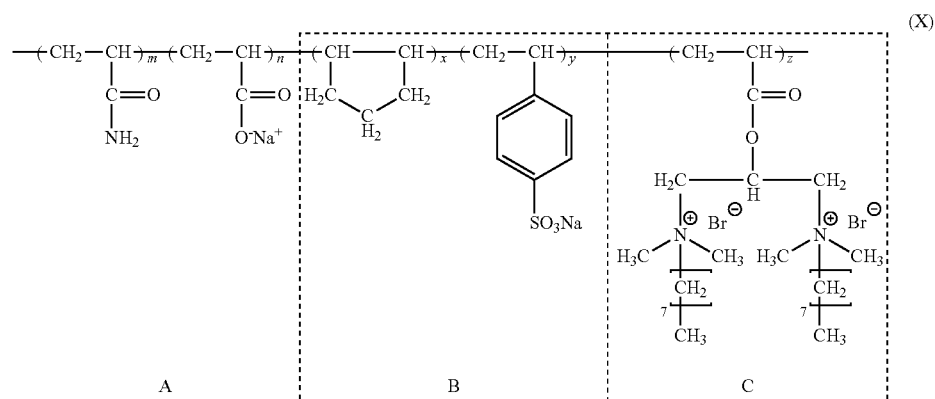
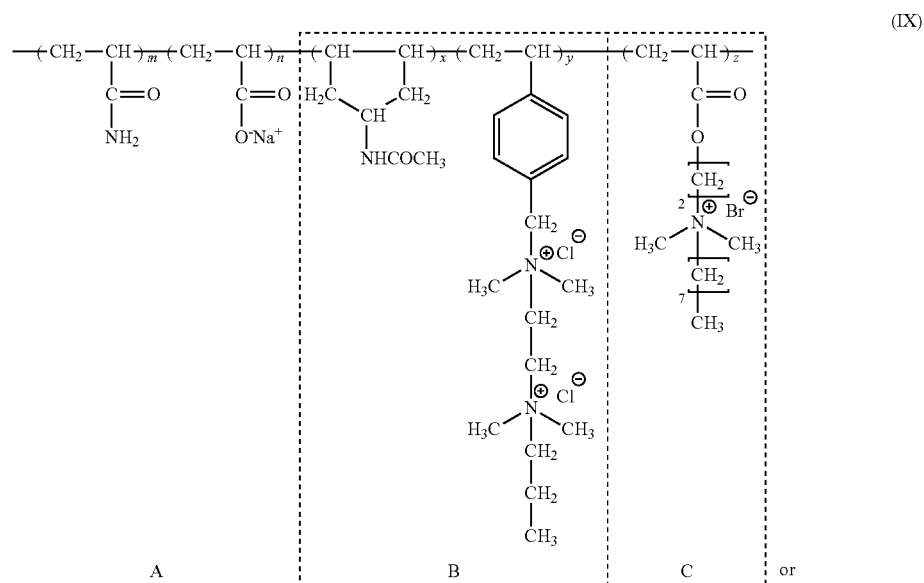
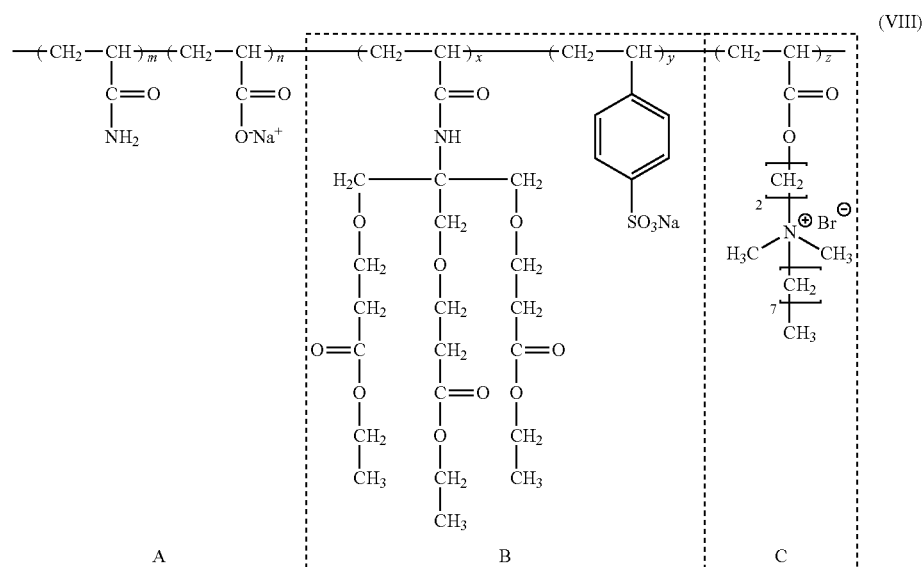
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The molecular weight of the amphiphilic macromolecule described above is between 1,000,000 and 20,000,000; preferably between 3,000,000 and 14,000,000.

The measurement of the molecular weight M is as follows: The intrinsic viscosity $[\eta]$ is measured by Ubbelohde viscometer as known in the art, then the obtained intrinsic viscosity $[\eta]$ value is used in the following equation to obtain the desired molecular weight M:

$$M=802 [\eta]^{1.25}$$

The amphiphilic macromolecule according to this present invention can be prepared by known methods in the art, for example, by polymerizing the structural unit for adjusting molecular weight, molecular weight distribution and charge characteristics, the highly sterically hindered structural unit and the amphiphilic structural unit in the presence of an initiator. The polymerization process can be any type well

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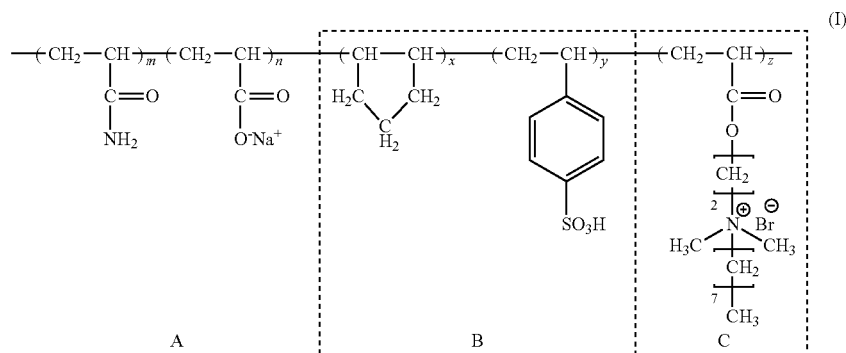
examples 1-5 of the invention in saline having a degree of mineralization of 3×10^4 mg/L at the concentration of 1750 mg/L

DETAILED DESCRIPTION OF THE INVENTION

The present invention is further illustrated below by combining specific examples; however, this invention is not limited to the following examples.

EXAMPLE 1

This example synthesized the amphiphilic macromolecule of formula (I):



known in the art, such as, suspension polymerization, emulsion polymerization, solution polymerization, precipitation polymerization, and etc.

A typical preparation method is as follows: the above monomers are each dispersed or dissolved in an aqueous system under stirring, the monomer mixture is polymerized by the aid of an initiator under nitrogen atmosphere to form the amphiphilic macromolecule. The so far existing relevant technologies for preparing an amphiphilic macromolecule can all be used to prepare the amphiphilic macromolecule of this invention.

All the monomers for preparing the amphiphilic macromolecule can be commercially available, or can be prepared on the basis of prior art technology directly; and some monomers' synthesis are described in details in specific examples.

DESCRIPTION OF FIGURES

FIG. 1 depicts the relationship of viscosity vs. concentration of the amphiphilic macromolecules obtained from examples 1-5 of the invention in saline having a degree of mineralization of 2×10^4 mg/L at a temperature of 80°C .

FIG. 2 depicts the relationship of viscosity vs. temperature of the amphiphilic macromolecules obtained from the

The synthesis of the amphiphilic macromolecule of this example was as follows:

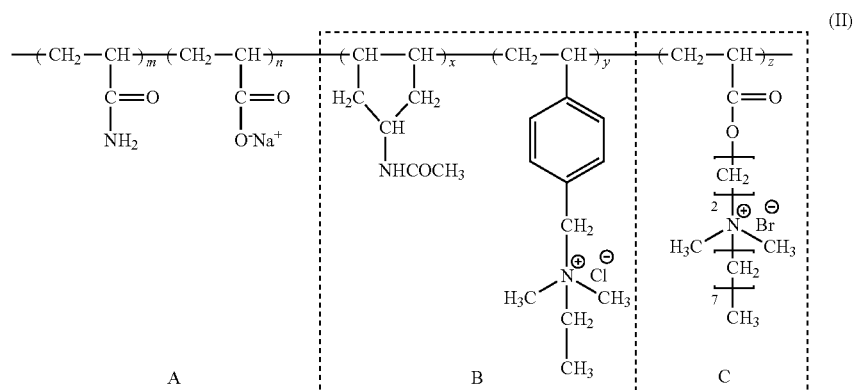
Firstly, water, accounting for $\frac{3}{4}$ of the total weight of the reaction system, was charged into a reactor, then various monomers, totally accounting for $\frac{1}{4}$ of the total weight of the reaction system, were charged into the reactor as well, and the molar percentages m, n, x, y, z for each repeating units were 78%, 20%, 0.25%, 0.5%, 1% in succession. The mixture was stirred until complete dissolution, and a pH adjusting agent was then added in to adjust the reaction solution to have a pH value of about 8, then nitrogen gas was introduced in for 30 minutes to remove oxygen contained therein. An initiator was added into the reactor under the protection of nitrogen gas, and nitrogen gas was further continued for 10 minutes, then the reactor was sealed. The reaction was conducted at a temperature of 22°C .; after 5 hours, the reaction was ended with a complete conversion. After the drying of the obtained product, powdered amphiphilic macromolecule was obtained. The molecular weight of the amphiphilic macromolecule was 1360×10^4 .

EXAMPLE 2

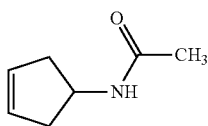
This example synthesized the amphiphilic macromolecule of formula (II).

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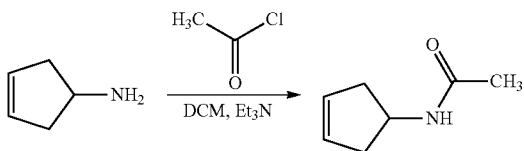
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The synthesis route of the monomer



was as follows:



The synthesis of the amphiphilic macromolecule of this example was as follows:

Firstly, water, accounting for 3/4 of the total weight of the reaction system, was charged into a reactor, then various

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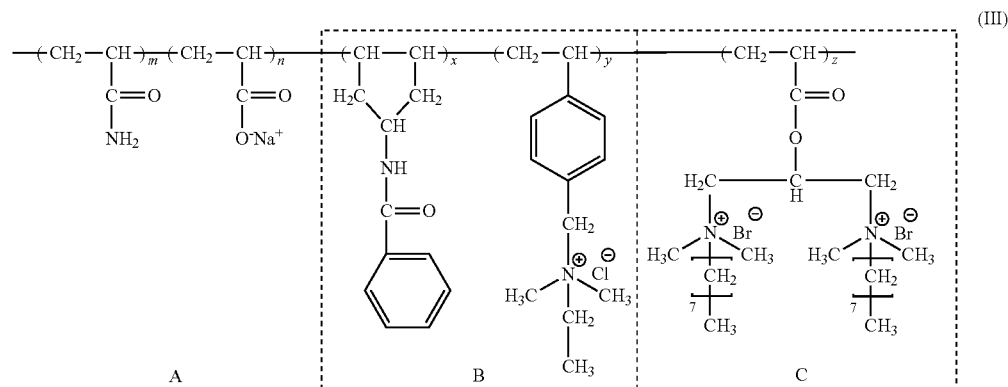
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monomers, totally accounting for 1/4 of the total weight of the reaction system, were charged into the reactor as well, and the molar percentages m, n, x, y, z for each repeating units were 73%, 25%, 0.15%, 0.15%, 1.7% in succession. The mixture was stirred until complete dissolution, and a pH adjusting agent was then added in to adjust the reaction solution to have a pH value of about 8, then nitrogen gas was introduced in for 40 minutes to remove oxygen contained therein. An initiator was added into the reactor under the protection of nitrogen gas, and nitrogen gas was further continued for 10 minutes, then the reactor was sealed. The reaction was conducted at a temperature of 25° C.; after 5 hours, the reaction was ended with a complete conversion. After the drying of the obtained product, powdered amphiphilic macromolecule was obtained. The molecular weight of the amphiphilic macromolecule was 1010×10⁴.

EXAMPLE 3

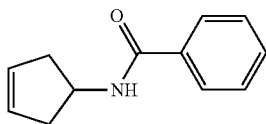
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This example synthesized the amphiphilic macromolecule of formula (III):

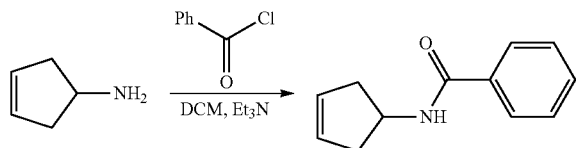


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The synthesis route of the monomer



was as follows:



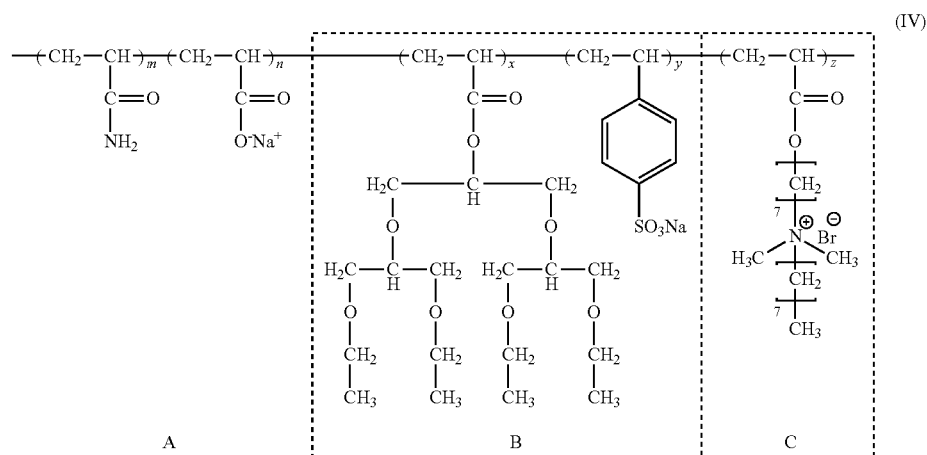
The synthesis of the amphiphilic macromolecule of this example was as follows:

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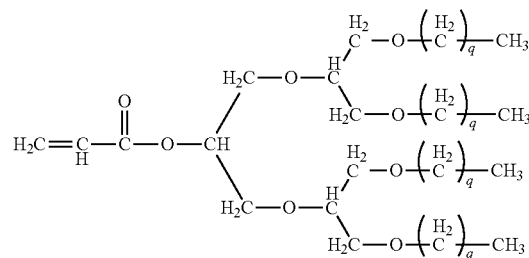
Firstly, water, accounting for $\frac{3}{4}$ of the total weight of the reaction system, was charged into a reactor, then various monomers, totally accounting for $\frac{1}{4}$ of the total weight of the reaction system, were charged into the reactor as well, and the molar percentages m, n, x, y, z for each repeating units were 75%, 24.5%, 0.15%, 0.15%, 0.2% in succession. The mixture was stirred until complete dissolution, and a pH adjusting agent was then added in to adjust the reaction solution to have a pH value of about 9, then nitrogen gas was introduced in for 30 minutes to remove oxygen contained therein. An initiator was added into the reactor under the protection of nitrogen gas, and nitrogen gas was further continued for 10 minutes, then the reactor was sealed. The reaction was conducted at a temperature of 25° C.; after 6 hours, the reaction was ended with a complete conversion. After the drying of the obtained product, powdered amphiphilic macromolecule was obtained. The molecular weight of the amphiphilic macromolecule was 660×10^4 .

EXAMPLE 4

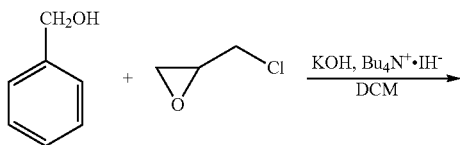
This example synthesized the amphiphilic macromolecule of formula (IV):



The synthesis route of the monomer

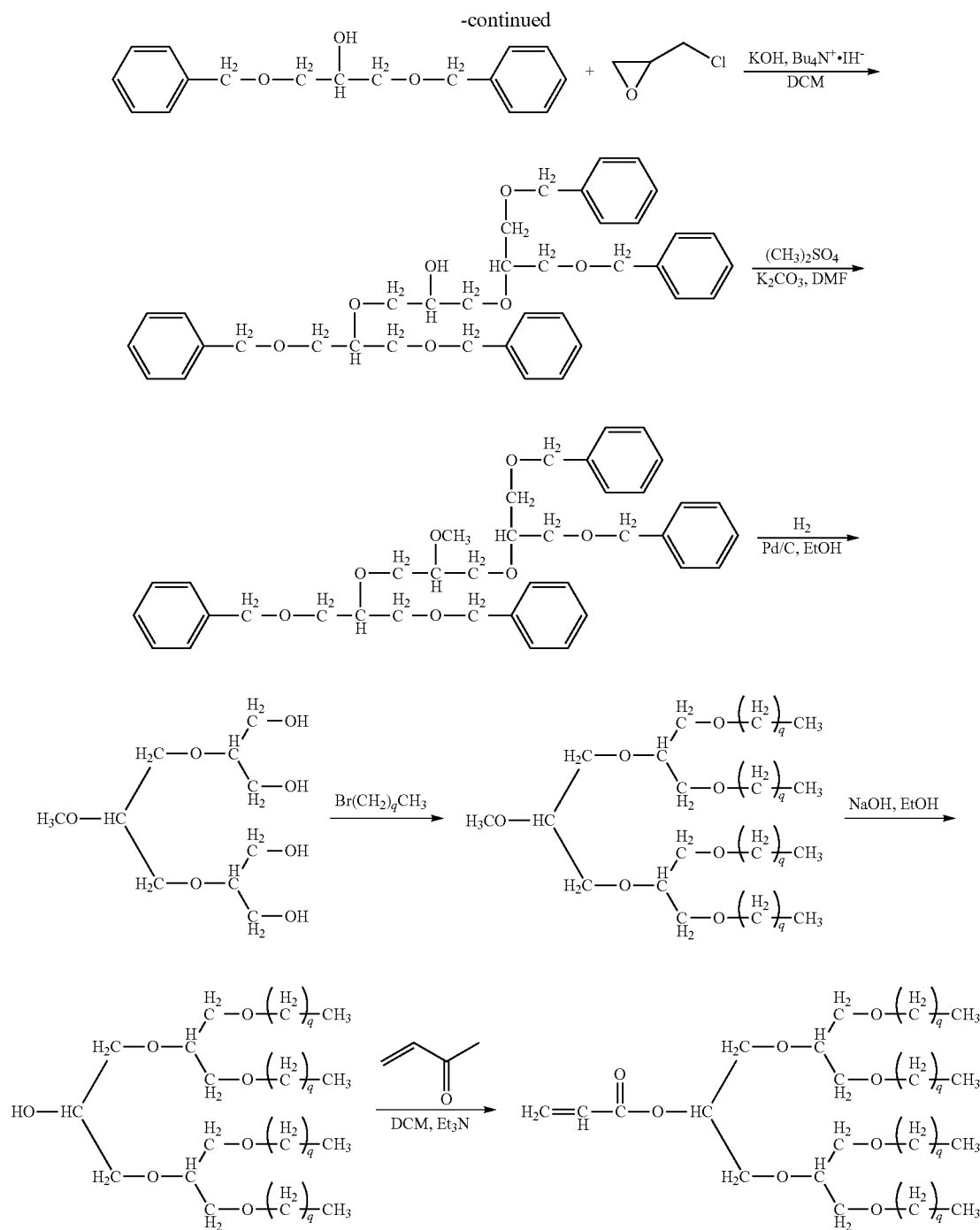


was as follows:



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was added into the reactor under the protection of nitrogen gas, and nitrogen gas was further continued for 10 minutes, then the reactor was sealed. The reaction was conducted at a temperature of 25° C.; after 6 hours, the reaction was ended with a complete conversion. After the drying of the obtained product, powdered amphiphilic macromolecule was obtained. The molecular weight of the amphiphilic macromolecule was 370×10^4 .

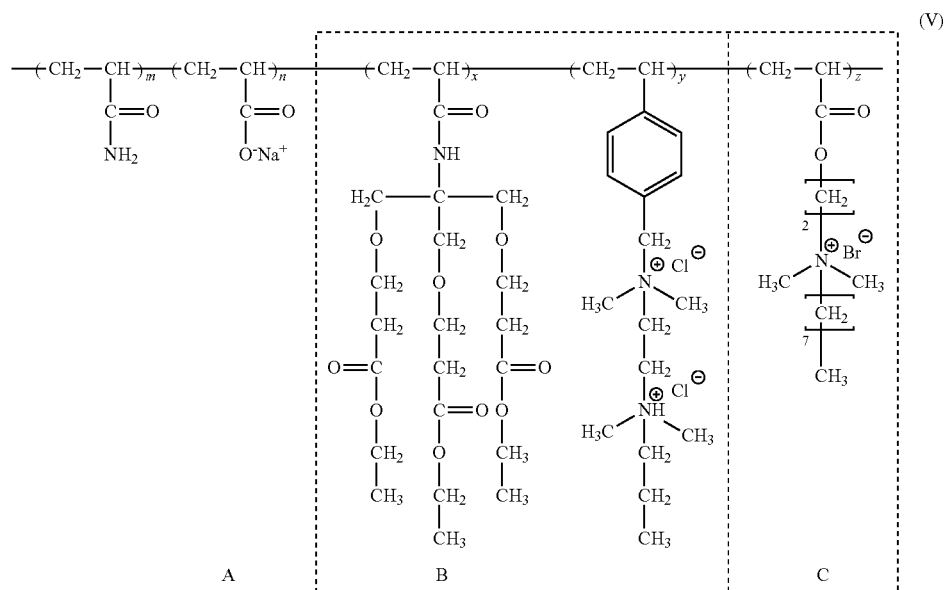
EXAMPLE 5

This example synthesized the amphiphilic macromolecule of formula (V):

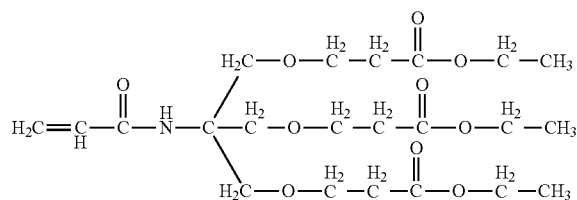
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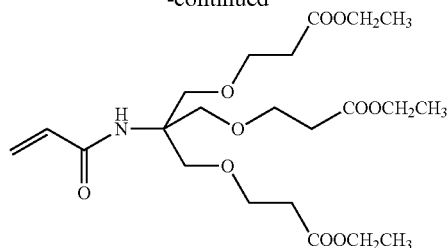
The synthesis route of the monomer



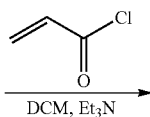
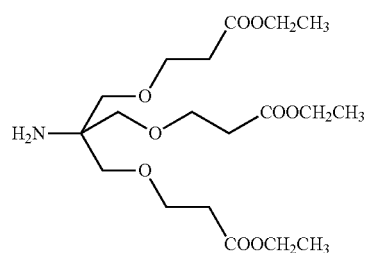
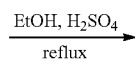
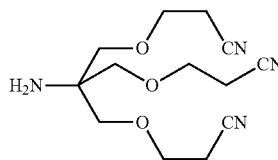
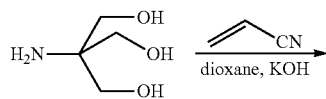
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-continued



was as follows:



The synthesis of the amphiphilic macromolecule of this example was as follows:

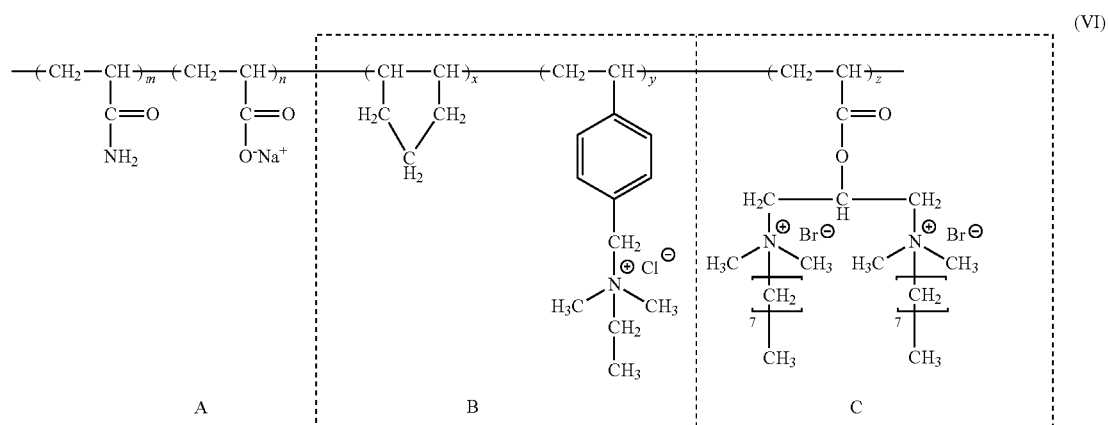
Firstly, water, accounting for $\frac{3}{4}$ of the total weight of the reaction system, was charged into a reactor, then various monomers, totally accounting for $\frac{1}{4}$ of the total weight of the reaction system, were charged into the reactor as well, and the molar percentages m, n, x, y, z for each repeating units were 78%, 21%, 0.1%, 0.1%, 0.8% in succession. The mixture was stirred until complete dissolution, and a pH adjusting agent was then added in to adjust the reaction solution to have a pH value of about 8, then nitrogen gas was introduced in for 30 minutes to remove oxygen contained therein. An initiator was added into the reactor under the protection of nitrogen gas, and nitrogen gas was further continued for 10 minutes, then the reactor was sealed. The reaction was conducted at a temperature of 25° C.; after 6 hours, the reaction was ended with a complete conversion. After the drying of the obtained product, powdered amphiphilic macromolecule was obtained. The molecular weight of the amphiphilic macromolecule was 450×10^4 .

EXAMPLE 6

This example synthesized the amphiphilic macromolecule of formula (VI):

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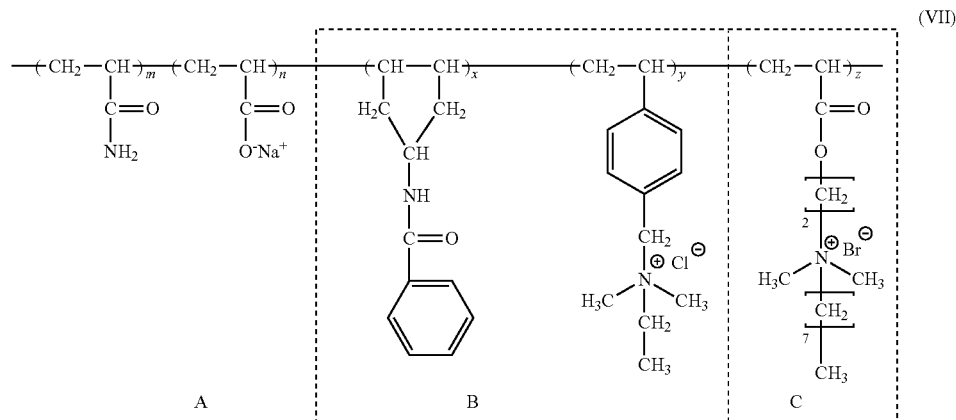


The synthesis of the amphiphilic macromolecule of this example was as follows:

Firstly, water, accounting for $\frac{3}{4}$ of the total weight of the reaction system, was charged into a reactor, then various monomers, totally accounting for $\frac{1}{4}$ of the total weight of the reaction system, were charged into the reactor as well, and the molar percentages m, n, x, y, z for each repeating units were 73%, 25%, 0.5%, 0.5%, 1% in succession. The mixture was stirred until complete dissolution, and a pH adjusting agent was then added in to adjust the reaction solution to have a pH value of about 8, then nitrogen gas was introduced in for 30 minutes to remove oxygen contained therein. An initiator was added into the reactor under the protection of nitrogen gas, and nitrogen gas was further continued for 10 minutes, then the reactor was sealed. The reaction was conducted at a temperature of 45°C .; after 3 hours, the reaction was ended with a complete conversion. After the drying of the obtained product, powdered amphiphilic macromolecule was obtained. The molecular weight of the amphiphilic macromolecule was 640×10^4 .

EXAMPLE 7

This example synthesized the amphiphilic macromolecule of formula (VII):



The synthesis of the amphiphilic macromolecule of this example was as follows:

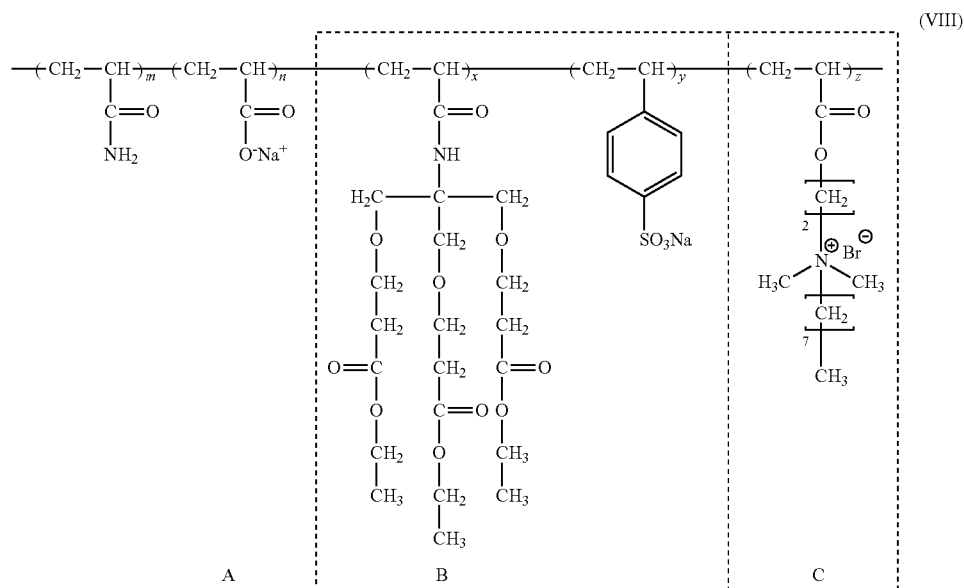
Firstly, water, accounting for $\frac{3}{4}$ of the total weight of the reaction system, was charged into a reactor, then various monomers, totally accounting for $\frac{1}{4}$ of the total weight of the reaction system, were charged into the reactor as well, and the molar percentages m, n, x, y, z for each repeating units were 75%, 23%, 0.25%, 0.5%, 1.25% in succession. The mixture was stirred until complete dissolution, and a pH adjusting agent was then added in to adjust the reaction solution to have a pH value of about 9, then nitrogen gas was introduced in for 30 minutes to remove oxygen contained therein. An initiator was added into the reactor under the protection of nitrogen gas, and nitrogen gas was further continued for 10 minutes, then the reactor was sealed. The reaction was conducted at a temperature of 55°C .; after 3 hours, the reaction was ended with a complete conversion. After the drying of the obtained product, powdered amphiphilic macromolecule was obtained. The molecular weight of the amphiphilic macromolecule was 107×10^4 .

EXAMPLE 8

This example synthesized the amphiphilic macromolecule of formula (VIII):

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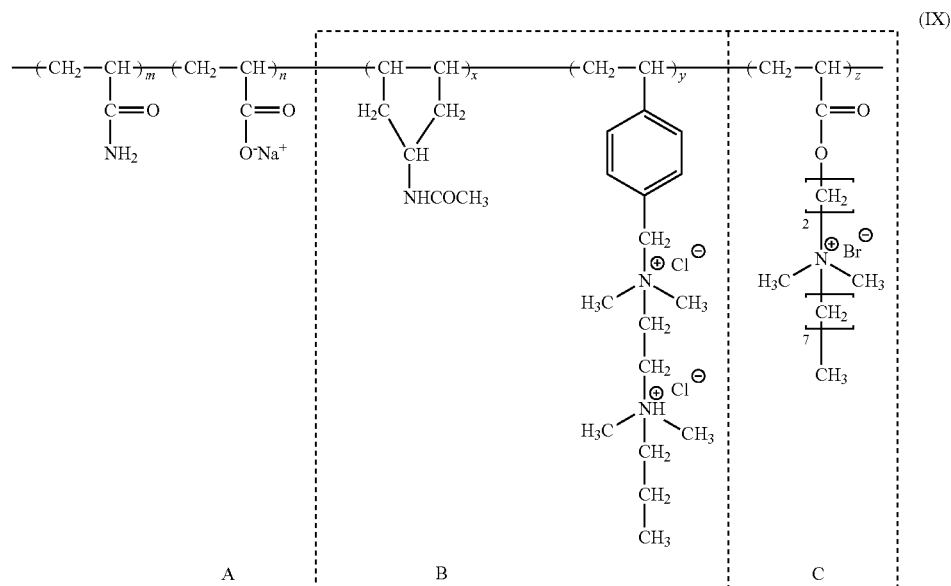
The synthesis of the amphiphilic macromolecule of this example was as follows:

Firstly, water, accounting for $\frac{3}{4}$ of the total weight of the reaction system, was charged into a reactor, then various monomers, totally accounting for $\frac{1}{4}$ of the total weight of the reaction system, were charged into the reactor as well, and the molar percentages m, n, x, y, z for each repeating units were 70%, 28%, 0.15%, 0.75%, 1.1% in succession. The mixture was stirred until complete dissolution, and a pH adjusting agent was then added in to adjust the reaction solution to have a pH value of about 8, then nitrogen gas was introduced in for 30 minutes to remove oxygen contained therein. An initiator was added into the reactor under the protection of nitrogen

gas, and nitrogen gas was further continued for 10 minutes, then the reactor was sealed. The reaction was conducted at a temperature of 55° C.; after 3 hours, the reaction was ended with a complete conversion. After the drying of the obtained product, powdered amphiphilic macromolecule was obtained. The molecular weight of the amphiphilic macromolecule was 310×10^4 .

EXAMPLE 9

This example synthesized the amphiphilic macromolecule of formula (IX):

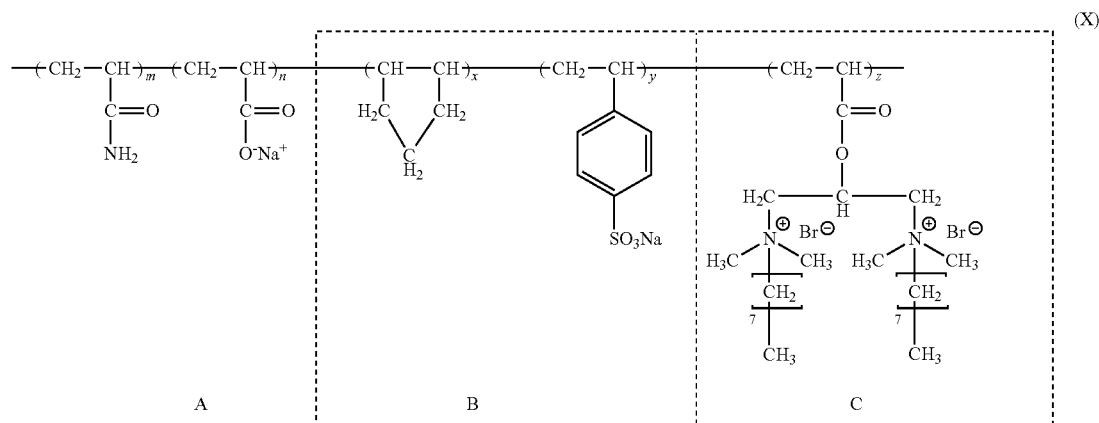


The synthesis of the amphiphilic macromolecule of this example was as follows:

Firstly, water, accounting for $\frac{3}{4}$ of the total weight of the reaction system, was charged into a reactor, then various monomers, totally accounting for $\frac{1}{4}$ of the total weight of the reaction system, were charged into the reactor as well, and the molar percentages m, n, x, y, z for each repeating units were 75%, 23.5%, 0.5%, 0.2%, 0.8% in succession. The mixture was stirred until complete dissolution, and a pH adjusting agent was then added in to adjust the reaction solution to have a pH value of about 8, then nitrogen gas was introduced in for 30 minutes to remove oxygen contained therein. An initiator was added into the reactor under the protection of nitrogen gas, and nitrogen gas was further continued for 10 minutes, then the reactor was sealed. The reaction was conducted at a temperature of 50°C .; after 2.5 hours, the reaction was ended with a complete conversion. After the drying of the obtained product, powdered amphiphilic macromolecule was obtained. The molecular weight of the amphiphilic macromolecule was 720×10^4 .

EXAMPLE 10

This example synthesized the amphiphilic macromolecule of formula (X):



The synthesis of the amphiphilic macromolecule of this example was as follows:

Firstly, water, accounting for $\frac{3}{4}$ of the total weight of the reaction system, was charged into a reactor, then various monomers, totally accounting for $\frac{1}{4}$ of the total weight of the reaction system, were charged into the reactor as well, and the molar percentages m, n, x, y, z for each repeating units were 75%, 23%, 0.5%, 0.5%, 1% in succession. The mixture was stirred until complete dissolution, and a pH adjusting agent was then added in to adjust the reaction solution to have a pH value of about 8, then nitrogen gas was introduced in for 30 minutes to remove oxygen contained therein. An initiator was added into the reactor under the protection of nitrogen gas, and nitrogen gas was further continued for 10 minutes, then the reactor was sealed. The reaction was conducted at a temperature of 50°C .; after 2 hours, the reaction was ended with a complete conversion. After the drying of the obtained product, powdered amphiphilic macromolecule was obtained. The molecular weight of the amphiphilic macromolecule was 520×10^4 .

MEASUREMENT EXAMPLES

Measurement Example 1

Saline having a mineralization degree of 2×10^4 mg/L was used to prepare amphiphilic macromolecule solutions with different concentrations, and the relationship between the concentration, temperature and the viscosity of the solution was determined. The results were shown in FIG. 1 and FIG. 2.

The figures showed that the amphiphilic macromolecule solutions of examples 1-5 still have favorable viscosifying capacity under the condition of high temperature and high degree of mineralization. The highly sterically hindered unit in the amphiphilic macromolecule reduced the rotational degree of freedom in the main chain and increased the rigidity of the macromolecule chain, which made the macromolecule chain difficult to curl and tend to stretch out, thus enlarging the hydrodynamic radius of the macromolecule; in the meantime, the amphiphilic structural unit associated each other to form the microdomain by intramolecular- or intermolecular-interaction, thus enhancing the viscosifying capacity of the solution remarkably under the conditions of high temperature and high salinity.

Measurement Example 2

Testing method: Under a testing temperature of 25°C ., 25 ml electric dehydration crude oil samples from three types of oilfields were added in a 50 ml test tube with a plug, then 25 ml aqueous solutions of amphiphilic macromolecule with different concentrations formulated with distilled water were added in. The plug of the test tube was tightened, then the test tube was shaken manually or by using an oscillating box for 80-100 times in horizontal direction, and the shaking amplitude should be greater than 20 cm. After sufficient mixing, the plug of the test tube was loosed. Viscosity reduction rate for crude oil was calculated according to the following equation:

$$\text{Viscosity reduction rate(\%)} = \frac{\text{viscosity of crude oil sample} - \text{viscosity after mixing}}{\text{viscosity of crude oil sample}} \times 100$$

TABLE 1

Experimental results of the heavy oil viscosity reduction of the amphiphilic macromolecule obtained from the example 6 to example 10 (oil-water ratio 1:1, 25° C.)							
oil-water volume ratio (1:1)		oil sample 1	viscosity reduction rate (%)	oil sample 2	viscosity reduction rate (%)	oil sample 3	viscosity reduction rate (%)
test temperature (25° C.)							
initial viscosity (mPa · s)		900	—	7400	—	12000	—
Example 6	400 mg/L	405	55.00	1900	74.32	3300	72.50
	600 mg/L	320	64.44	1350	81.76	2450	79.58
	800 mg/L	275	69.44	1040	85.95	1250	89.58
	1000 mg/L	245	72.78	740	90.00	850	92.92
	1200 mg/L	220	75.56	670	90.95	725	93.96
Example 7	400 mg/L	475	47.22	2100	71.62	3500	70.83
	600 mg/L	375	58.33	1750	76.35	2600	78.33
	800 mg/L	290	67.78	1475	80.07	1350	88.75
	1000 mg/L	230	74.44	1050	85.81	900	92.50
	1200 mg/L	230	74.44	805	89.12	775	93.54
Example 8	400 mg/L	535	40.56	1690	77.16	3150	73.75
	600 mg/L	460	48.89	1100	85.14	1900	84.17
	800 mg/L	390	56.67	780	89.46	1125	90.63
	1000 mg/L	350	61.11	690	90.68	850	92.92
	1200 mg/L	330	63.33	630	91.49	710	94.08
Example 9	400 mg/L	470	47.78	1800	75.68	3600	70.00
	600 mg/L	390	56.67	1480	80.00	2400	80.00
	800 mg/L	310	65.56	975	86.82	1370	88.58
	1000 mg/L	260	71.11	675	90.88	1025	91.46
	1200 mg/L	230	74.44	580	92.16	840	93.00
Example 10	400 mg/L	505	43.89	1600	78.38	3800	68.33
	600 mg/L	425	52.78	1150	84.46	2350	80.42
	800 mg/L	350	61.11	825	88.85	1275	89.38
	1000 mg/L	315	65.00	695	90.61	1000	91.67
	1200 mg/L	280	68.89	625	91.55	825	93.13

Table 1 showed that the amphiphilic macromolecules of examples 6-10 had good effects for viscosity reduction as to all three oil samples. With the increase of the concentration of the amphiphilic macromolecule solution, the viscosity reduction rate increased. And, when the concentration of the amphiphilic macromolecule solution was the same, the viscosity reduction rate increased with the enhancing of the viscosity of the oil sample. It was believed that the amphiphilic macromolecule could reduce the viscosity of the crude oil remarkably via a synergetic effect between the highly sterically hindered structural unit and the amphiphilic structural unit, which could emulsify and disperse the crude oil effectively.

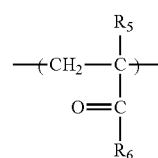
Industrial Application

The amphiphilic macromolecule of this invention can be used in oilfield drilling, well cementing, fracturing, crude oil gathering and transporting, sewage treating, sludge treating and papermaking, and it can be used as intensified oil producing agent and oil displacing agent, heavy oil viscosity reducer, fracturing fluid, clay stabilizer, sewage treating agent, retention aid and drainage aid and strengthening agent for papermaking.

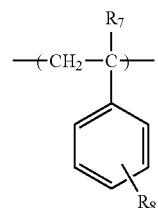
The amphiphilic macromolecule of this invention is especially suitable for crude oil exploitation, for instance, it can be used as an intensified oil displacement polymer and a viscosity reducer for heavy oil. When it is used as an oil displacement agent, it has remarkable viscosifying effect even under the condition of high temperature and high salinity, and can thus enhance the crude oil recovery. When it is used as a viscosity reducer for heavy oil, it can remarkably reduce the viscosity of the heavy oil and decrease the flow resistance thereof in the formation and wellbore by emulsifying and dispersing the heavy oil effectively.

What is claimed is:

1. An amphiphilic macromolecule comprising, as repeating units, a structural unit A for adjusting molecular weight, molecular weight distribution and charge characteristics, a sterically hindered structural unit B and an amphiphilic structural unit C, wherein the sterically hindered structural unit B comprises a structure G and a structure of formula (4), wherein the structure G is a cyclic hydrocarbon structure formed on the basis of two adjacent carbon atoms in the main chain, or is selected from a structure of formula (3):



formula (3)



formula (4)

wherein in formula (3), R₅ is H or a methyl group; R₆ is a radical selected from the group consisting of the structures of formula (5) and formula (6):

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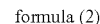
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7. The amphiphilic macromolecule as claimed in claim 1, wherein the structural unit A for adjusting molecular weight, molecular weight distribution and charge characteristics has a structure of formula (2);

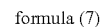


8. The amphiphilic macromolecule as claimed in claim 1, wherein the cyclic hydrocarbon structure formed on the basis of the two adjacent carbon atoms in the main chain is selected from the group consisting of:

8. The amphiphilic macromolecule as claimed in claim 1, wherein the cyclic hydrocarbon structure formed on the basis of the two adjacent carbon atoms in the main chain is selected from the group consisting of:



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in formula (7), the definition of G is as described in claim 1; the definitions of R₇ and R₈ are as described in formula (4); x and y respectively represent the molar percentages of the structural units in the entire amphiphilic macromolecule, and x is from 0.02 to 2 mol %, y is from 0.05 to 5 mol %.

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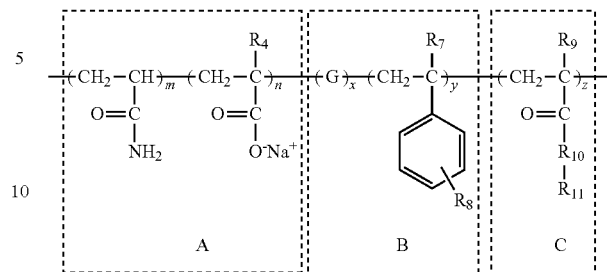
10. The amphiphilic macromolecule as claimed in claim 3, wherein R_{10} and R_{11} may be selected from $-\text{O}(\text{CH}_2)_g\text{N}^+(\text{CH}_3)_2(\text{CH}_2)_h\text{CH}_3\text{X}^-$, $-\text{NH}(\text{CH}_2)_i\text{N}^+(\text{CH}_3)_2(\text{CH}_2)_j\text{CH}_3\text{X}^-$, $-\text{O}(\text{CH}_2)_k\text{N}^+((\text{CH}_2)_p\text{CH}_3)_3\text{X}^-$, $-\text{O}(\text{CH}_2)_q\text{N}^+(\text{CH}_3)_2(\text{CH}_2)_\alpha\text{CH}(\text{SO}_3\text{H})\text{CH}_2(\text{EO})_\beta(\text{PO})_\gamma(\text{CH}_2)_\delta\text{CH}_3\text{X}^-$, $-\text{NH}(\text{CH}_2)_q\text{N}^+(\text{CH}_3)_2(\text{CH}_2)_\alpha\text{CH}(\text{SO}_3\text{H})\text{CH}_2(\text{EO})_\beta(\text{PO})_\gamma(\text{CH}_2)_\delta\text{CH}_3\text{X}^-$, $-\text{O}(\text{CH}_2)_q\text{N}^+(\text{CH}_3)_2(\text{CH}_2)_\alpha\text{CH}(\text{COOH})\text{CH}_2(\text{EO})_\beta(\text{PO})_\gamma(\text{CH}_2)_\delta\text{CH}_3\text{X}^-$, $-\text{NH}(\text{CH}_2)_q\text{N}^+(\text{CH}_3)_2(\text{CH}_2)_\alpha\text{CH}(\text{COOH})\text{CH}_2(\text{EO})_\beta(\text{PO})_\gamma(\text{CH}_2)_\delta\text{CH}_3\text{X}^-$, $-\text{O}(\text{CH}_2)_2\text{N}^+(\text{CH}_3)_2(\text{CH}_2)_\epsilon\text{SO}_3^-$, $-\text{OCH}(\text{CH}_2\text{N}^+(\text{CH}_3)_2(\text{CH}_2)_\zeta\text{CH}_3\text{Cl}^-)\text{CH}_2)_\eta\text{O}(\text{CH}_2)_\theta\text{CH}_3$, $-\text{OCH}(\text{CH}_2\text{N}^+(\text{CH}_3)_2(\text{CH}_2)_\lambda\text{CH}_3\text{Cl}^-)\text{CH}_2)_\tau\text{O}(\text{CH}_2)_\kappa\text{CH}_3$, $-\text{OCH}(\text{CH}_2\text{N}^+(\text{CH}_3)_2(\text{CH}_2)_r\text{CH}_3\text{X}^-))_2$, $-\text{OCH}(\text{CH}_2\text{N}^+(\text{CH}_2)_s\text{CH}_3)_3\text{X}^-))_2$;

wherein g, i, k and q are respectively integers from 1 to 6; h and j are respectively integers from 3 to 21; p is an integer from 3 to 9; α is an integer from 1 to 12; β and γ are respectively integers from 0 to 40; δ is an integer from 0 to 21; ϵ is an integer from 4 to 18; ζ is an integer from 1 to 21; η and τ are respectively integers from 1 to 30; θ and κ are respectively integers from 3 to 21; λ is an integer from 0 to 9; r is an integer from 3 to 21; s is an integer from 3 to 9; and X^- is Cl^- or Br^- .

11. The amphiphilic macromolecule as claimed in claim 1, wherein the amphiphilic macromolecule has a structure of formula (9):

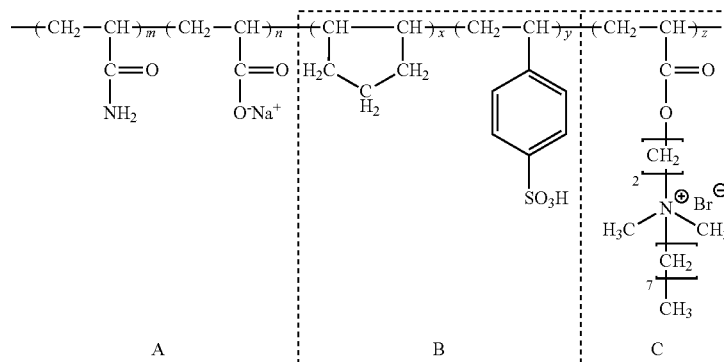
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formula (9)

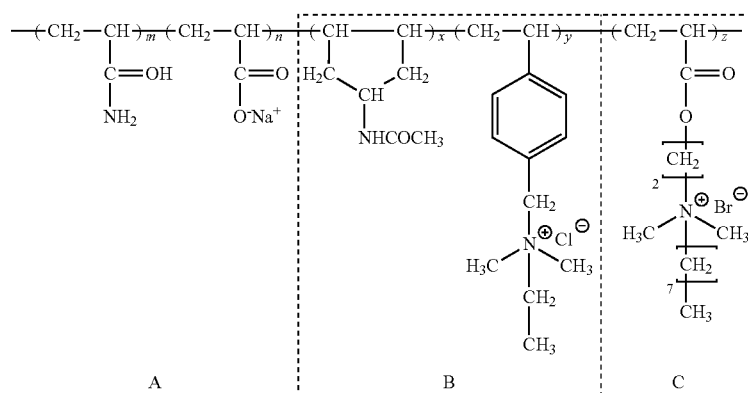


wherein in formula (9), R_4 is selected from the group consisting of H and a methyl group; m and n represent the molar percentages of the structural units in the entire amphiphilic macromolecule, and m is from 70 to 99 mol %; n is from 1 to 30 mol %; the definitions of G, R_7 , R_8 , x and y are as described in formula (7); R_9 is H or a methyl group, R_{10} is $-\text{O}-$ or $-\text{NH}-$; R_{11} is a radical containing a straight-chain hydrocarbyl, a branched hydrocarbyl, a polyoxyethylene (PEO), a polyoxypropylene (PPO), an EO-PO block, a mono-quaternary ammonium salt, a multiple-quaternary ammonium salt, or a sulfonic acid and salts thereof; z represents the molar percentage of the structural unit in the entire amphiphilic macromolecule, and z is from 0.05 to 10 mol %.

12. The amphiphilic macromolecule as claimed in claim 1, which is a compound of formulas (I)-(X):

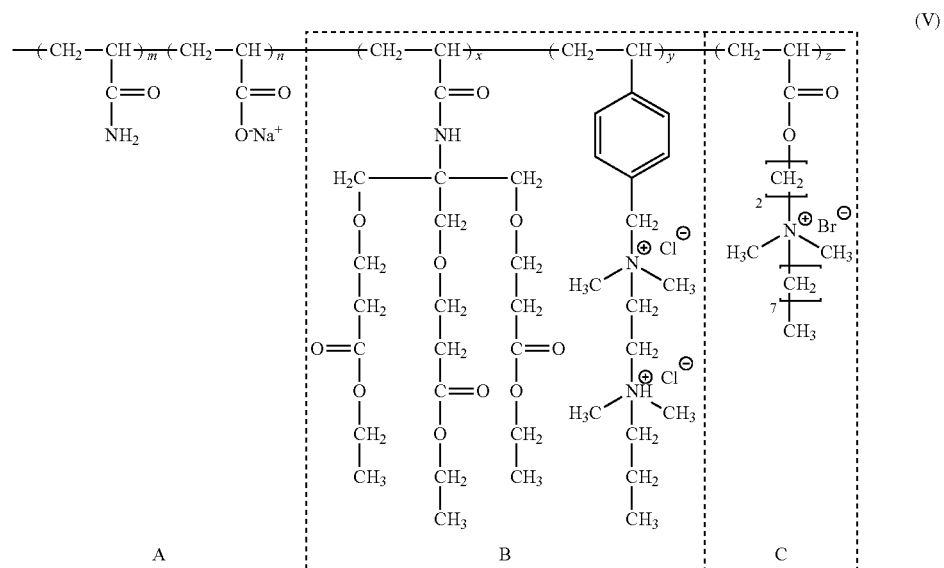
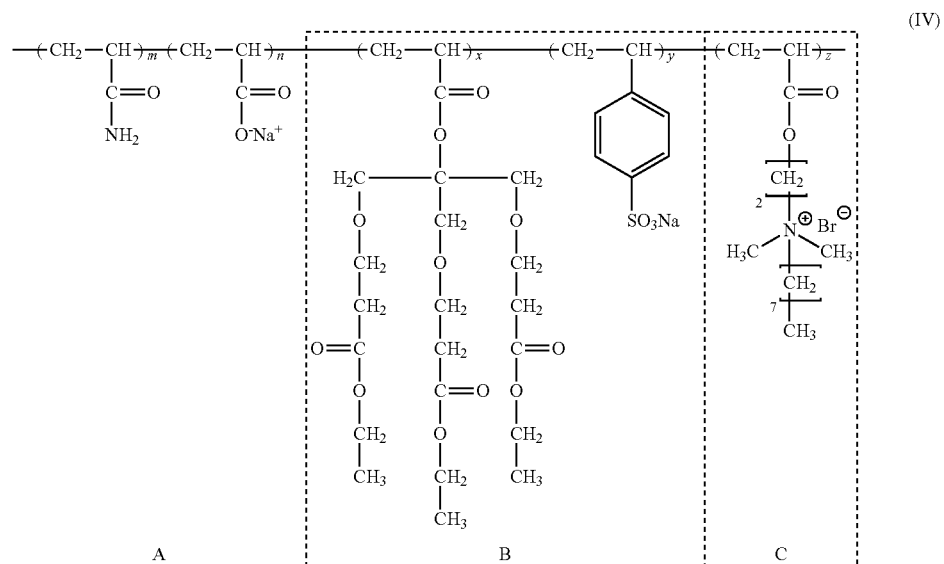
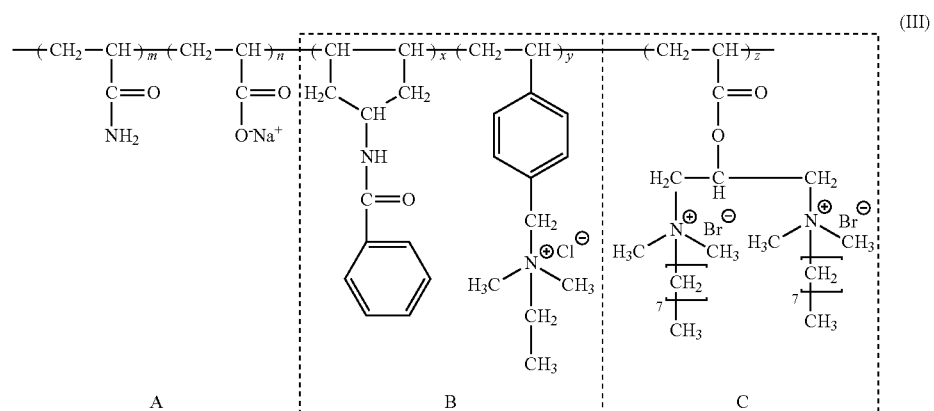


(I)

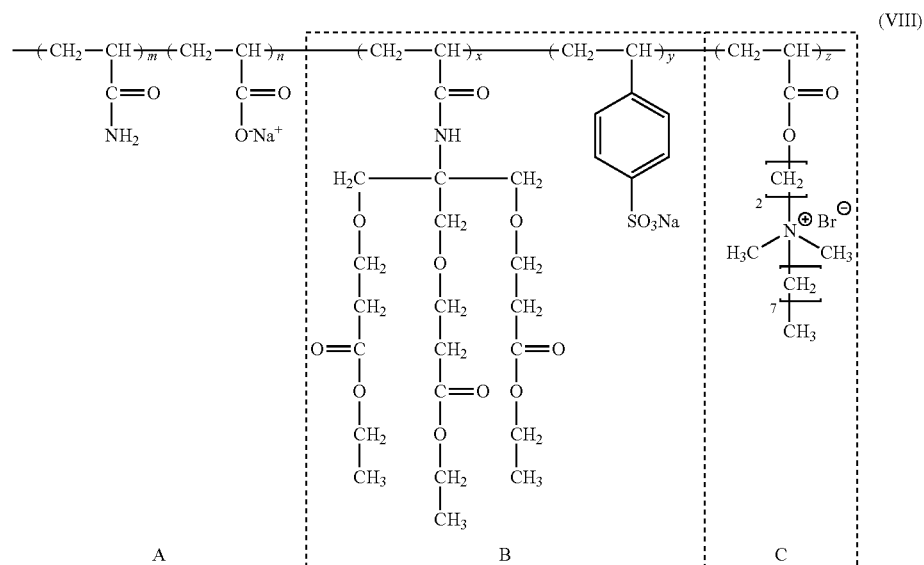
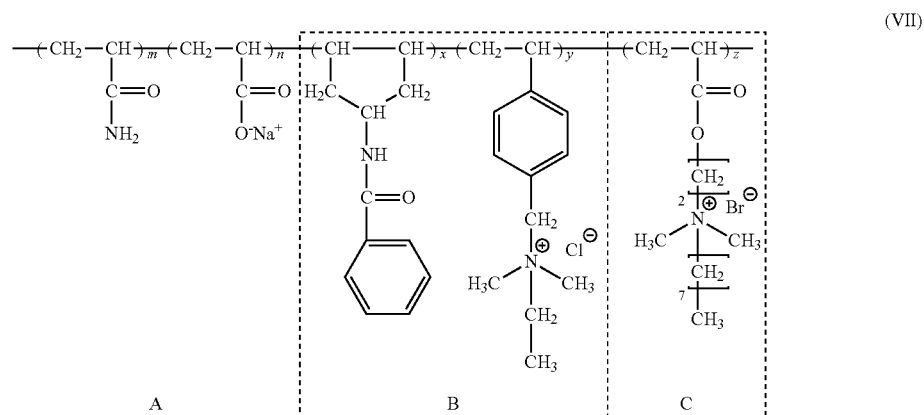
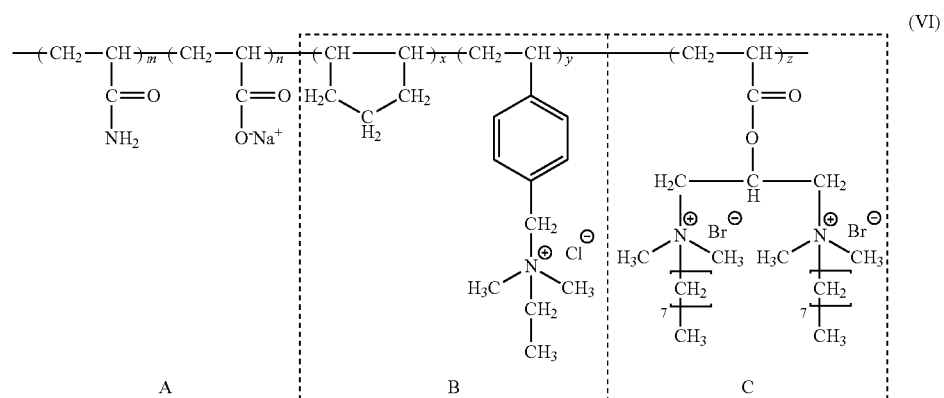


(II)

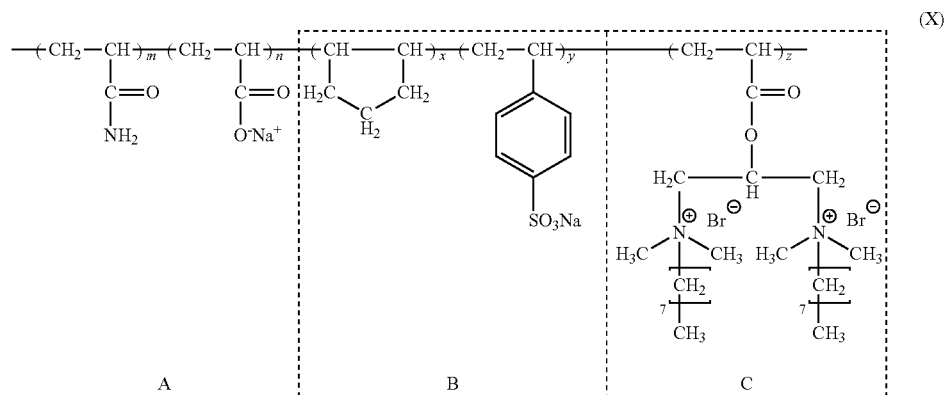
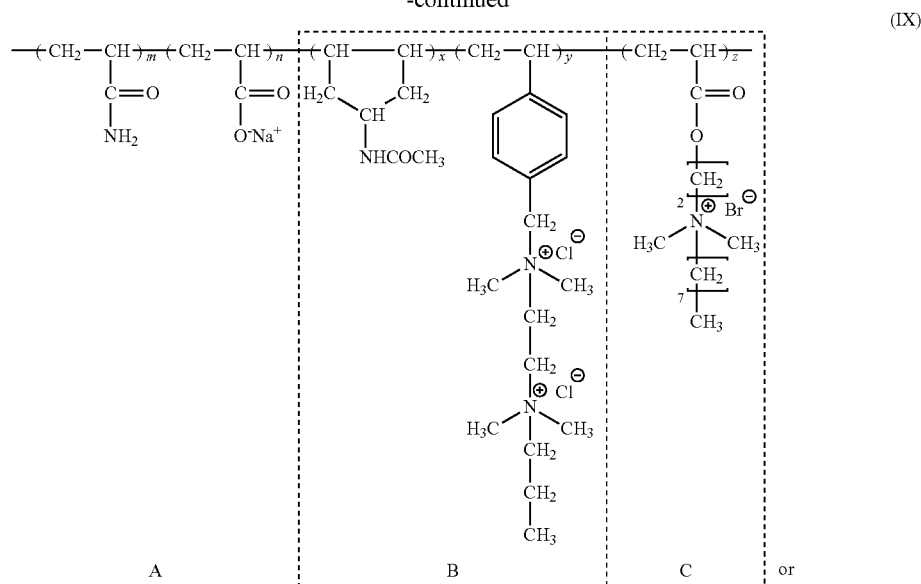
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13. The amphiphilic macromolecule as claimed in claim 1, wherein the amphiphilic macromolecule has a viscosity average molecular weight of between 1000000-20000000.

14. A method comprising: formulating the amphiphilic macromolecule as claimed in claim 1 into an aqueous solution: and

utilizing the aqueous solution in oilfield drilling, well cementing, fracturing, crude oil gathering and transporting, sewage treating, sludge treating and papermaking as

intensified oil producing agent and oil displacing agent, or as a heavy oil viscosity reducer, fracturing fluid component, clay stabilizer, sewage treating agent, retention aid and drainage aid or strengthening agent for paper-making.

15. The amphiphilic macromolecule as claimed in claim 1, wherein R_5 is H.

* * * * *